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Incidence of milling energy on dry-milling attributes of rice starch modified by planetary ball milling

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ABSTRACT

Rice starch was modified in a planetary mill. The effects of milling energy (E) on physicochemical and functional properties were investigated. Particle size, crystallinity degree and gelatinization enthalpy were reduced with the increase of milling energy. The effect of E on particle size reduction could be predicted by generalized Holmes´ model. Heat dissipation was evidenced during milling through the non-linear relationship between size reduction ratio and milling energy. Hydration and pasting properties were significantly affected. Water soluble index (WSI) and swelling power (SP) increased with increasing both energy and temperature of hydration test. For the greatest energy and temperature level (85ºC), WSI value varied between 1.5-29.7% and SP value between 7.4-16.4g/g, relative to native starch. The crystallinity showed negative relationships with WSI and a SP. Regards to pasting properties, peak viscosity (PV) decreased from 4384 mPa.s to 544

mPa.s as E varied between 0 kJ/g and 4.08 kJ/g. Peak, setback and final viscosities parameters showed a linear relationship with the particle size. There were found strong correlations between physicochemical and functional properties of modified starches, which evidenced the dependence of the modification on milling severity. Planetary ball milling is presented as an eco-friendly alternative to modify native rice starch properties.

Keywords: grinding energy, crystallinity, particle size, high impact mill, functional properties.

1. INTRODUCTION

Starch is one of the most abundant carbohydrates in plants. Particularly, rice starch constitutes 90% (w/w) of milled rice and it has the characteristic of being gluten-free and thus, suitable for the elaboration of products intended for celiac people. Starches are widely used as food ingredients to improve appearance, texture, and overall acceptability of foodstuffs and they are characterized by their great versatility for applications in the food and beverage industry. The use of starches allows the simplification of labeling by substituting certain additives, reducing formulation costs and ensuring some texture attributes in the final product (Taggart, 2004). However, starches have some limitation for their application, due to the tendency to retrogradation and low solubility in water, which restrict their functional properties. For this reason, they are rarely consumed and industrially used in the native state, and there is a need to modify them to improve the positive attributes and to exclude the shortcomings of the native starches (Alcázar-Alay & Meireles, 2015; Guerzoni, Gianotti, & Vernocchi, 2011).

The starch modification industry is in constant progress. Different methods have been developed: chemical, physical and enzymatic or combinations of them; to carry out changes in the starch functionality. However, there is an increasing tendency in the use of physical methods due to their simplicity, low cost and their contribution to food safety because of the absence of chemical or biological agents (Ashogbon & Akintayo, 2014). High-pressure treatment, gamma irradiation, microwave use and high-impact milling (Błaszczak et al., 2007; Deka & Sit, 2016; He et al., 2014; Zhu, 2016) are some examples of the current physical methods applied, with little or no waste production, as alternatives to modify the physicochemical properties of starches. Among high-impact milling methods, the planetary ball mill is presented as a novel technology recently applied to cereals and their derivatives by dry and wet milling at laboratory scale (He et al., 2014; María A. Loubes & Tolaba, 2014). At industrial scale, planetary ball mills for continuous operation (up to five tons of powder per hour) are available only for mineral grinding (Technics and Technology of Disintegration Co., 2015).

It has been found that grinding in planetary ball mill can achieve significant modifications in the morphology and crystalline structure of the starch granules, giving them changes in physicochemical properties, useful for various industrial applications. The degree of modification given by the planetary ball mill depends on both the intensity of the process and the nature of the starch, and is associated with the distortion of the ordered structure and the increase of the amorphous phase (Tan et al., 2015). Some researchers have shown that the alteration conferred by the planetary mill can reach not only strictly crystalline regions, but also double-helix structures located in less ordered areas (Liu, Ma, Yu, Shi, & Xue, 2011).

The structural modifications, changes in particle size distribution and starch damage, resulting from the milling process, are reflected in changes in hydration and pasting properties of starch suspensions (Barrera et al., 2013; Chiang & Yeh, 2002; Hossen et al., 2011; Zhang, Zhao, & Xiong, 2010).

Literature reports show a constant interest to investigate starch behavior during food processing as well as to evaluate the aptitude of starch as functional ingredient in different food products (Wani et al., 2012). However, there are currently no publications on starch grinding in high-impact mills, where the energy used for the process is exposed. Instead, the milling time and the rotation speed are often reported which are strongly dependent on the type and capacity of the selected mill. The use of specific milling energy would facilitate the process simulation by using energy-particle size milling models (Rhodes, 2008). Size reduction by milling is an operation with high energy consumption and low efficiency. A measure of the efficiency of the operation is based on the energy required to create a new surface (McCabe, Smith, & Harriot, 2007). With the postulates of Rittinger´s, Kick´s and Bond´s laws, it is possible to predict the needed energy to generate a determined particle size reduction. Moreover, there have been attempts to generate a single equation to predict the performance of various materials during milling, such as Holmes´ and Hukki´s models (Rhodes, 2008).

Therefore, the aim of the present work was to study the potential of the planetary ball mill to obtain physically modified rice starch and to produce improvements in its physicochemical properties, as a function of the grinding energy. The aptitude of the general milling equation to describe the energy-size relationship was also evaluated. The modifications achieved in the crystalline structure and particle size distribution of the starch, and their impact on the hydration and pasting properties were investigated.

2. MATERIALS AND METHODS

2.1. Materials

Native rice starch of food grade (Remy B7, Beneo GmbH, Germany) was supplied by Saporiti S.A. (Buenos Aires, Argentina). The amylose content of the rice starch was 18.4 g/100 g of total starch, determined according to an iodine binding-based method of Li, Wang, and Zhu (2016). Chemical composition (dry basis) of rice starch was provided by the manufacturer as follows: 88.7% carbohydrates (by difference), 13.7% moisture, 1.0% protein, 0.0% lipid, 0.2% ash.

2.2. Dry milling treatment

The pulverization of rice starch was performed in a planetary ball mill model PM 100 manufactured by Retsch (Retsch GmbH, Germany) with zirconium jar (500 mL) and balls (diameter: 5 mm) at different levels of milling energy within 0.26 – 4.08 kJ/g and constant rotational speed of 400 rpm. Milling energy represents the energy provided to the content of the milling jar (sample and balls); therefore, a previous calibration was required using an empty jar (energy at “ralenti”). The milling protocol involved pauses of 40 min each 10 min of grinding, by this procedure the overheating of the starch was avoided, and the sample temperature never exceeded 55°C (values of sample temperature are reported in Table 1). A change in the rotational direction of the jar was established every 30 seconds. Starch sample (115 g) and five times weight balls were placed into the grinding jar up to about two thirds of its capacity according to method reported by Loubes (2015). Native rice starch

was adopted as control sample. Moisture content was determined by triplicate after milling treatment, according to (AOAC, 2000). It decreased as the milling energy increased from 12.8% (d.b.) to 10.8% (d.b.), for 0.26 kJ/g and 4.08 kJ/g, respectively.

2.3. Particle size distribution

Particle size distribution was determined by static light scattering (SLS) in a Mastersizer 2000 device (Malvern Instruments Ltd., Worcestershire, UK), equipped with a dispersion unit Hydro 2000MU. The pump was operated at 1800 rpm. Bi-distilled water was used as dispersing agent for which diffraction index and absorptivity were 1.53 and 0.001 respectively. The instrument provides size distribution parameters in terms of volumetric fraction: D_{10}, D_{50} (median) and D_{90} (corresponding to the diameters of 10%, 50% and 90% of cumulative frequency respectively). From the equipment´s software (Malvern Application v5.60, Malvern Instruments Ltd., Worcestershire, UK) the specific surface area (SSA), the mean volumetric diameter (D4.3) and the "Span" index (Eqn. 1), as a measure of size dispersion, were obtained. The particle sizes are reported as the average of five readings made on a sample.

$$\text{Span} = (D_{90} - D_{10})/D_{50} \qquad \text{(Eq. 1)}$$

2.4. Energy – size milling models

The generalized model proposed by Holmes (1957) was used to simulate the relationship between the specific milling energy (E) and the particle size (x), for which the postulates of

Rittinger´s, Kick´s and Bond´s laws are presented as special cases and assume the value of *n* as 2, 1 and 1.5, respectively:

$$dE/dx = - c\,(1/x^n) \qquad \text{(Eq. 2)}$$

Such equation suggests that the energy required to produce a small change in the size of unit mass can be expressed as a power function of the size of the material (Barbosa-Cánovas, Ortega-Rivas, Juliano, & Yan, 2005).

If D_{50} is adopted as a measure of x the integrated form of the equation yields:

$$\int_0^E dE = - C \int_{D50i}^{D50f} (1/D_{50}^{\,n}) \qquad \text{(Eq. 3)}$$

$$E = (c/(1-n))\,(D_{50i}^{\,1-n} - D_{50f}^{\,1-n}) \qquad \text{(Eq. 4)}$$

Where E is the specific energy required to pulverize the particle from D_{50i} (initial diameter: median of native starch) to D_{50f} (final diameter: median of modified starch). The parameters of the model: *n* and *c* can be obtained by regression analysis from experimental data (E "versus" D_{50f}). For *n* equal to 2 the generalized equation becomes to Rittinger model which has been successfully applied to model ultra-fine grinding (Rhodes, 2008).

Linear and non-linear relationships between the specific milling energy and the size reduction ratio ($R_r = D_{50i} / D_{50f}$) have been also used to follow the milling operation (Barbosa-Cánovas et al., 2005; Rhodes, 2008).

Regression analyses were performed using the Statgraphics Centurion (version XVI, Statistical graphics Corporation, Inc., Virginia, USA) statistical software.

2.5. X-ray diffraction

X-ray diffraction analysis were performed using a Philips diffractometer model X'Pert MPD (PANalytical B.V., Netherlands) under Kα-radiation of copper (λ = 0.154 nm). The scanning region of the diffraction angle (2θ) was 6-32° and the scanning speed was set at 0.9º/min. The iterative method developed by Roa, Santagapita, Buera, and Tolaba (2014) was adopted in order to set a baseline for the scattering and to calculate the total and amorphous areas which were quantified using OriginPro Software version 8.0 (OringinLab Corporation, Northampton, EE. UU.). The crystallinity degree (CD) was calculated as the ratio between the crystalline and the amorphous areas, obtained from the diffraction patterns, according to:

$$CD\ (\%) = 100*(TA-AA)\ /TA \qquad \text{(Eq. 4)}$$

Where TA, AA are the total and amorphous areas, respectively, and (TA-AA) represents the area corresponding to crystalline peaks. Mean and standard deviation values of duplicates are reported.

2.6. Thermal properties

Thermal properties were determined by differential scanning calorimetry (DSC), in a Mettler-Toledo DSC calorimeter, model 822 (Schwerzenbach, Switzerland).

For the analysis, 6 mg of each sample was weighed exactly in Mettler pan of 160 µl capacity and bi-distilled water was added in a starch:water ratio of 1:3 (m/v). Subsequently, the pan was sealed and equilibrated for 24 hours at room temperature before performing the calorimetric test, which was carried out with a heating cycle comprised between 25°C and 100°C, with a constant heating rate of 10°C/minute, taking an empty pan as reference.

The resulting thermograms were analyzed with the STARe Software software version 6.1 (Mettler Thermal Analysis) to obtain the peak temperature (Tp) and the enthalpy of gelatinization (ΔH), which was calculated from the integration of the endothermic transition curve. The thermal parameters were recorded in triplicate.

2.7. Hydration properties

Swelling power (SP) and water solubility index (WSI) were determined in triplicate, according to the methodology described by Vandeputte et al. (2003), with some modifications. The starch (1 g, dry basis) was dispersed in 30 ml of distilled water and heated for 30 minutes while stirring, in a thermostatic bath at 55 ° C, 65 ° C, 75 ° C or 85 ° C. It was then centrifuged at 700 x g for 15 minutes. The supernatant was removed and dried at 105ºC to constant weight. The dry sample weight, dry supernatant weight and sediment weight were recorded to calculate SP and WSI, as follows:

$$WSI\ (\%) = (dy\ supernatant\ weight / dry\ sample\ weight) * 100 \quad \text{(Eq. 5)}$$

$$SP\ (g/g) = sediment\ weight / (dry\ sample\ weight - dry\ supernatant\ weight) \quad \text{(Eq. 6)}$$

2.8. Pasting profile

Pasting properties of starch samples were determined using a Rapid Visco Analyser RVA 4500 (Perten Instruments, Australia). Starch (3.5 g) was dispersed in 25 g of distilled water contained in an aluminum pan which was subjected to a controlled heating-cooling cycle. Thermal cycle involved an initial thermal equilibration at 50°C (1 min) followed by dynamic heating at 12.5ºC/min, while stirring at 160 rpm, up to 95°C. Then the sample was held at 95°C (2.5 min) and finally it was cooled to 50°C at 12ºC/min and maintained at 50°C (2 min). The following parameters were obtained from the pasting curve, using the software Thermocline, Versión 3.15 (Perten Instruments, Macquarie Park, Australia): initial pasting temperature (PT), peak viscosity (PV), peak time (Pt), breakdown (BD), trough viscosity (TV), setback (SB) and final or cool paste viscosity (FV). Measurements were performed in duplicate.

2.9. Statistical analysis

Analysis of variance (ANOVA), regression and correlation analyses (correlation coefficients from the matrix of Pearson) were performed using the statistical program Statgraphics Centurion version XVI (Statistical graphics Corporation, USA), comparing the means by the least significant difference test of Fisher (LSD), with a confidence level of 95 or 99%.

3. RESULTS AND DISCUSSION

3.1. Milling energy

232 In the present work the mill was operated at a constant rotational speed of 400 rpm and the
233 energy involved in the grinding of rice starch in the planetary ball mill was linearly
234 increased with the grinding time (R^2 = 0.9996) as it can be appreciated in Table 1. Due to
235 Coriolis effect, a significant reduction of processing time can be achieved by using the
236 planetary ball mill in comparison with traditional ball milling (Retsch, 2009).

237

238 **3.2. Particle size**

239 Particle size distribution of control was bimodal with the volumetric fraction of the peak at
240 148.3 μm higher than that of peak at 28.2 μm. In contrast, monomodal size distributions
241 were observed for grinded starches. Peaks at 10.7 and 12.3 μm were found by using 0.26
242 and 0.52 kJ/g respectively. Such peaks presented a shoulder on the right denoting a residual
243 fraction of starch particles with a larger size. However, with a further increase of milling
244 energy the shoulder disappears. A symmetric and well defined peak at 12 μm was observed
245 using 1.04 kJ/g or higher milling energies. Particle size converged to this asymptotic peak
246 value as milling energy increases within the experimental range.
247 Characteristic parameters: median (D_{50}), specific surface area (SSA) and "Span" index
248 which were obtained from particle size distribution are showed in Table 1, as function of
249 milling energy. D_{50} values of modified rice starches were significantly lower than that of
250 control due to the drastic reduction of particle size as a consequence of high impact milling.
251 The significant reduction of "Span" index (up to 49% compared to the control) with
252 increasing milling energy evidenced the potential of planetary ball mill to produce a very
253 homogeneous granulometry. The specific surface area of the modified starches was higher
254 than that of control. The highest value of SSA (0.62 m^2/g) was obtained with a non-severe

255 milling condition (0.26 kJ/g, equivalent to 5.4 minutes at 400 rpm); this represents an
256 increase of 114% over the control. With further treatment SSA was decreased, anyway it
257 never fell below the control value. A similar effect was found by Che, Li, Wang, Dong
258 Chen, and Mao (2007) during pulverization of cassava starch in a vacuum ball-mill. These
259 authors attributed the SSA reduction to a dynamic equilibrium between large particles
260 crushing into smaller ones and tiny particles agglomerating. Agglomeration is favored by
261 the great surface energies provided by the high impact milling.
262 In contrast to high-pressure treatment or ultra-sonication method (BeMiller, 2018;
263 Błaszczak et al., 2007; Deka & Sit, 2016; He et al., 2014; Mohammad Amini, Razavi, &
264 Mortazavi, 2015; Zhu, 2016) which are carried out with water as vapor or liquid media, the
265 dry milling here proposed avoid the dehydration step to obtain powder starch. Ultra-
266 sonication as well as microwave or irradiation techniques (ref-1; Deka & Sit, 2016; He et
267 al., 2014) are emerging technologies still of high cost to be applied for starch modification
268 at industrial scale.

269

270 **3.3. Energy – size relationships**

271 The significant effect of milling energy (0 - 1.99 kJ / g) on particle size reduction can be
272 observed in Figure 1. Generalized milling equation, with *c* constant equal to 940.9
273 kJ/[mg*$\mu m^{(1-n)}$] and *n* equal to 5.6 (dimensionless), is shown and the good agreement
274 between the experimental values and those predicted by the Holmes´ model (R^2 = 0.9635)
275 can be also appreciated. It must be noted that by doing the regression by setting *n* equal to
276 2, as established by the Rittinger model, the adjustment was less satisfactory (R^2 = 0.7499).
277 In order to have a good fit, only the energy values between 0 and 1.99 kJ/g were considered

for the regression analysis. At higher energies the model did not adjust due to the negligible decrease of particle size (asymptote of the curve).

This model assumes that the energy is proportional to the new surface created. Therefore, the deviation from the predicted values would indicate that part of the milling energy is lost due to heat dissipation phenomenon (Barbosa-Cánovas et al., 2005; Loubes, 2015; Rhodes, 2008).

Recently Loubes (2015) reported that the magnitude of heat dissipation in a planetary ball mill is dependent on rotation speed. Thus, by selecting a convenient speed, the thermal events were minimized to obtain, as a consequence, a linear relationship among energy and size reduction ratio. Shashidhar, Murthy, Girish, and Manohar (2013), who studied the hammer milling of coriander seeds, also found a linear E – R_r dependence.

In this work, the occurrence of significant heat dissipation seems to be corroborated by the non-linear dependence (R^2 = 0.9805) that was found between the specific milling energy and the size reduction ratio:

$$E = 0.0047\exp(1.036R_r) \qquad (7)$$

In accordance with this result, Mohd Rozalli, Chin, and Yusof (2015) accounted an exponential E- R_r relationship for milling of peanut using an ultra-high speed mill.

To conclude, the deviation from the Rittinger model or a non-linear E – R_r relationship can be considered as an evidence of the irreversible heat dissipation in high impact milling where the energy delivered to the jar´s content is not exclusively used for the reduction of the particle size.

3.4. Crystallinity

The native and modified starches presented typical A-type crystalline patterns (Fig. 2) with diffraction peaks (2θ) at 15º, 17º, 18º and 23º; which are characteristic of cereal starches (Singh, Singh, Kaur, Singh Sodhi, & Singh Gill, 2003; Zhang et al., 2010; Zobel, 1988). X-ray peak intensities of samples diminished as the treatment energy rose. Starches treated at energies higher than 1.99 kJ/g showed a diffuse pattern. This behavior reflects the decrease in the crystalline portion of the granules and the consequent increase of the amorphous fraction as the grinding progresses.

The crystallinity degree at different milling energies is also shown in Fig. 2. The CD of the control sample was 46%. This value could be reduced by 30% with the lowest energy condition (0.26 kJ/g) and 86% with the most drastic conditions (1.99-4.08 kJ/g). The minimum CD reached was 6%. From 1.99 kJ/g, no significant differences ($p < 0.05$) were observed in the crystallinity. CD variation of modified starches was related to the grinding energy through a potential model ($CD\% = 12.47\ E^{-0.624}$; $R^2 = 0.9657$).

These results indicated that dry milling in the planetary ball mill was able to generate different degrees of change in rice starch structure, depending on the severity of the treatment. In agreement with Martínez-Bustos, López-Soto, San Martín-Martínez, Zazueta-Morales, and Velez-Medina (2007), ball milling treatment induced to spatial disorder of amylopectin and amylose, caused by a rise in the temperature due to conduction or dissipation of the mechanical energy during ball milling.

3.5. Thermal properties

Table 1 shows the values of the gelatinization parameters, peak temperature and enthalpy of gelatinization, of rice starch samples subjected to different milling energies. All the samples

showed thermograms with a single endothermic peak, characteristic of gelatinization processes with a high water content (Biliaderis, Maurice, & Vose, 1980).

The crystallinity degree and the proportion of amylose and amylopectin chains influence the gelatinization temperature. Gelatinization temperature is an important property to be determined in cereals, because it is strongly related to the cooking time and the final texture of the cooked products (Champagne, 2004). As it can be seen in Table 1, Tp values suffered a shift towards lower temperatures as milling progressed. This trend was also found by J.-J. Chen, Lii, and Lu (2003), Huang, Xie, Chen, Lu, and Tong (2008), María A. Loubes and Tolaba (2014) and Roa (2015) when performing mechanical treatments by grinding rice starch, cassava and corn starch, rice flour and amaranth flour; respectively.

As explained by Singh et al. (2003), differences in transition temperatures can be associated with the difference in the crystallinity degree of the samples. High transition temperatures are attributed to a high degree of crystallinity, which provides the granule structural stability and makes it more resistant to gelatinization. It is in agreement with the correlation found ($r = -0.9820$; $p < 0.01$) between ΔH and CD.

ΔH values were reduced from 11.57 J/g (native starch) to 1.53 J/g for the sample treated at 0.54 kJ/g. These results evidence that the crystalline structure and the double helix structure of the rice starch were damaged by the mechanical treatment (Han, Chang, & Kim, 2007; Martínez-Bustos et al., 2007), since ΔH is a general measure of crystallinity and it is an indicator of the loss of molecular order within the granule (Singh et al., 2003). From 1.04 kJ/g onwards no endothermic peaks were detected and it was found, therefore, that the starch samples were completely gelatinized.

The results show that the mechanical modification by grinding allows converting the structure of the starch from a semi-crystalline state to an amorphous state. It generates a

349 decrease in the values of gelatinization enthalpy and peak temperature, without the need to
350 add water and to dry the product later, taking advantage of hydrothermal pre-gelatinization
351 treatments.
352 Unlike extrusion cooking, where the complete gelatinization of starch occurred
353 (Hagenimana, Ding, & Fang, 2006; Menegassi, Pilosof, & Arêas, 2011) high impact ball
354 milling can produce starch with slight or severe thermal damage, partial or total loss of
355 crystallinity (amorphous starch). By means of adequate process conditions and milling
356 protocol the degree of starch modification could be well controlled.
357

358 **3.6. Hydration properties**

359 WSI and SP indexes, for the different milling energy and temperature conditions of the
360 hydration test are shown in Table 2. Dry-milling led to a significant increase in water
361 hydration properties of rice starch. WSI and SP values of milled starches were always
362 higher than those of the native starch, at the same temperature. The highest values
363 corresponded to the most severe grinding condition in all the tests. For the highest energy
364 and temperature levels (4.08 kJ/ g and 85°C), the WSI value varied between 0.07-29.70 %
365 and SP between 2.12- 16.38 g/g in comparison with the control at the lowest temperature (0
366 kJ/g and 55°C). For energies greater than 1.99 kJ/g changes in SP were comparatively
367 lower than those observed in the range 0-1.99 kJ/g. A non-linear SP-E relationship was
368 accounted (not shown). In contrast, a linear relationship between WSI and E (R^2> 0.97)
369 were found for all temperatures tested. Moreover, an increase in the hydration properties
370 was observed with the increase of the test temperature at a fixed grinding energy. The
371 highest WSI and SP values were found at the highest test temperature (85ºC). The

information obtained on the hydration properties can be useful at the time of designing a grinding treatment to obtain starches for specific applications.

The hydration behavior of modified rice starches demonstrated a close relationship with the integrity and crystallinity of starch granules, in agreement with literature reports (C.-J. Chen, Shen, & Yeh, 2010; Chiang & Yeh, 2002; Devi, Fibrianto, Torley, & Bhandari, 2009; He et al., 2014). As shown in Figure 3 (a and b), CD showed a negative exponential relationship (R^2> 0.9) with solubility and a negative linear relationship (R^2> 0.9) with SP. From these results, it can be inferred that increasing the proportion of the amorphous phase (greater disorder), facilitates water intake and its interaction with the polymer chains, favoring the solubility of the starch granules in water and promoting their swelling capacity.

3.7. Pasting properties

The RVA records and parameters of native and mechanically activated rice starches are shown in Fig. 4 and Table 3, respectively.

The pasting properties of modified rice starches were significantly affected ($p<0.05$) by milling energy. When the mechanical activation increased, PT, PV, BD, TV, SB and FV values decreased, which was similar to several literature reports concerning to different milling techniques applied to rice starch (J.-J. Chen et al., 2003; Devi et al., 2009; Zhang et al., 2010). Significant correlations ($p<0.01$) between milling energy and PV (r = -0,9161), BD (r = -0,9869), TV (r = -0,8709), SB (r = -0,9420) and FV (r = -0,9059) were found. These relationships demonstrate the capacity of the planetary ball mill to modify the

394 physicochemical properties of rice starch, under the selected conditions of rotational speed
395 and milling energy.
396 Pasting temperature of native rice starch in the present study (79.1ºC ± 0,1ºC) is within the
397 reported range (63.80ºC to 95.10ºC) for rice starches isolated from non-waxy rice varieties
398 (Wani et al., 2012). In comparison with control (native starch), rice starches processed with
399 milling energies within 0.52 and 1.99 kJ/g showed lower values of pasting temperature
400 (70.6°C – 76.2°C). Modified starches can swell and absorb water more rapidly than native
401 starch, promoting starch gelatinization and the increase of viscosity at lower temperature
402 (Asmeda, Noorlaila, & Norziah, 2016; Tan et al., 2015). In contrast, between 2.63 and 4.08
403 kJ/g, PT values were higher (84.8 – 94.0°C) than that of control. A similar result was found
404 by Barrera et al. (2013) who detected an increase in PT records for wheat starch processed
405 in a disk mill, relative to native starch.
406 Peak viscosity reflects the water retention capacity of starch granules. Starches pulverized
407 in the planetary ball mil presented PV values within 544 – 3627 mPa.s; these values were
408 lower than that of native starch (4387 Pa.s). By increasing the content of damaged starch,
409 the starch acquires less resistance to the swelling of the granules, resulting in smaller PV
410 (Asmeda, Noorlaila, & Norziah, 2016).
411 No differences were found among BD values of native starch and starches modified with
412 energies within 0.26 - 0.52 kJ/g. This result evidenced a cooking behavior similar to control
413 sample for these modified rice starches. Good palatability and quality during cooking are
414 strongly associated to high values of BD (Kesarwani, Chiang, & Chen, 2016). Thus,
415 according to this criterion, the best results in the present work were those obtained at low
416 milling energies.

417 During cooling step, a new increment in apparent viscosity called setback viscosity (70 –
418 229% respect to TV) took place as result of retrogradation tendency of amylose chains. SB
419 is an useful parameter related to the texture of the final product (Wani et al., 2012).
420 FV indicates the starch capacity to form a viscous paste after being cooked and cooled.
421 Modified starches showed values of FV within 526 ± 42 mPa.s and 4792 ± 46 mPa.s, such
422 values were significantly lower than that of native starch (5764 ± 46 mPa.s). For control
423 sample and starches processed between 0.26 and 1.5 kJ/g the values of FV were higher than
424 those of PV, and the increments were in the range 23 to 31%. In contrast, the value of FV
425 was slightly lower than that of PV (reduction of 1 – 3%) in the case of modified starches at
426 1.99 - 4.08 kJ/g. Hossen et al. (2011) also obtained FV values higher than PV and a
427 reduction in final viscosity values by increasing the milling severity during rice starch
428 grinding using a co-jet mill. These authors attributed the reduction to the small particles
429 that lose the ability to form gels after being cooked and cooled.
430
431 **3.8. Effect of particle size reduction on pasting properties**

432 Peak and setback viscosity as well as final viscosity presented a linear relationship (R^2 >
433 0,92) with median particle size (D_{50}) (Fig. 5).
434 A significant and positive correlation was found between PV and D50 ($r = 0.87$; $p < 0.01$)
435 for modified starches; the linear relationship among the mentioned variables revealed that
436 size reduction is associated to decrease of viscosity. The same behavior was found by
437 Hossen et al. (2011) for starches from different sources, including rice starch. According
438 with Tan et al. (2015), the viscosity loss is due to the small size of swelled granule. In the

present work, D_{50} of modifies rice starches also presented a significant correlation with SB ($r = 0.84$; $p < 0.01$) and with FV ($r = 0.89$; $p < 0.01$).

It must be noted that these relationships are confined within 0.26 and 1.99 kJ/g. At higher levels of milling energy nonlinear relationships were obtained (not shown) due to the asymptotic tendency of D_{50} as the milling severity increased.

3.9. Correlations between structural and functional properties

The Pearson coefficient varies from 1 to -1; it is a measure of the tendency of two variables to decrease or increase together. A correlation coefficient of zero means to have two independent variables. Based on coefficients from Pearson matrix, it was found the following significant correlations ($p < 0.01$) for modified starches (E = 0.26 – 4.08 kJ/g):

(a) Crystallinity - hydration properties at 85ºC: CD-WSI ($r = -0.76$), CD-SP ($r = -0.95$)

Hydration capacity enhanced with crystallinity degree decreasing.

(b) Crystallinity – pasting properties: CD-PV ($r = 0.95$), CD-SB ($r = 0.92$), CD-FV ($r = 0.95$).

The ability of modified starches to form paste diminished as crystallinity decreased.

(c) Thermal - pasting or hydration properties at 85ºC: ΔH-PV ($r = 0.82$), ΔH-SB ($r = 0.75$), ΔH-FV ($r = 0.82$), ΔH-SP ($r = -0.86$).

As gelatinization degree of modified starches increased the aptitude to form paste decreased.

(d) Particle size – hydration properties at 85ºC: D_{50}-WSI ($r = -0.96$; for the energy range of 0.26-1.99 kJ/g), D_{50}-SP ($r = -0.97$), SSA-WSI ($r = -0.89$), SSA-SP ($r = -0.82$).

A reduction of particle size favored the hydration of starch particles. However, this result cannot be attributed to the increase of specific surface area due to SSA was increasing only within 0 – 0.26 kJ/g energy range, as discussed in section 3.2.

(e) Particle size – pasting properties: D50-PV (r = 0.87), D50-SB (r = 0.84), D50-FV (r = 0.89), SSA-PV (r = 0.92), SSA-SB (r = 0.88), SSA-FV (r = 0.91).

Size reduction can be associated to decrease of viscosity. A detailed discussion was presented in section 3.7.

4. CONCLUSIONS

This work showed that dry milling in a planetary ball mill is especially suitable to produce structural changes in rice starch, which significantly affect its behavior. It was possible to modify the physicochemical and functional properties of the native rice starch, without the generation of waste products during the process. However, planetary ball mills are now available only at laboratory-scale. Further research will be required for scaling starch milling using industrial-scale equipment.

The proposed method was effective to reduce both particle size and size dispersion as well as to increase the specific surface area of starch samples. Pasting properties of modified starches showed significant differences in comparison with native rice starch, even those samples processed at low milling energies. However, no significant effect of milling energy on pasting parameters was detected above 3.56 kJ/g and 4.08 kJ/g. It was also possible to obtain amorphous starch and starch with different crystallinity degrees by the appropriate selection of grinding conditions.

By increasing the severity of the milling treatment and the temperature of the hydration tests the hydration properties increased. The higher absorption capacity and solubility in water presented by the modified starches in relation to the control, give them distinctive characteristics to perform cooking and sensorial attributes of bread and pasta products.

In accordance to RVA tests, the modified rice starch, despite of its poor capacity to form paste, could be applied to produce starch gels for starch-thickened sauces.

As a result of its fine granulometry, modified rice starch has a mouth feel similar to fat globule and therefore it could be used as fat-replacer in low-fat foods. Due to its high solubility, it could facilitate the elaboration of homogeneous and viscous liquid suspensions which are valued in liquid food formulations.

In summary, rice starch treatment by planetary ball mill, allow modifications of several structural and functional characteristics that extend their possible applications in the cosmetic, pharmaceutical and food industry.

5. ACKNOWLEDGMENTS

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638 **Figure captions**

639 **Figure 1:** relationship between grinding energy and particle diameter D50. (□):
640 experimental data, (-): predicted by the generalized Holmes´ equation, (-): predicted by the
641 Rittinger model.

642

643 **Figure 2.** Spectra of X-ray diffraction and crystallinity degree (CD) of control and
644 modified rice starches, depending on the specific energy of grinding.

645

646 **Figure 3.** Relationship between the crystallinity degree (CD, %) and a) the water solubility
647 index (WSI, %), b) the swelling power (SP, g/g); depending on the temperature of the
648 hydration test.

649 a) **55ºC**: WSI = 191.81 $CD^{1.19}$; **65ºC**: WSI = 176.29 $CD^{1.17}$; **75ºC**: WSI = 126.41 $CD^{0.92}$;

650 **85ºC**: WSI = 125.31 $CD^{0.89}$

651 b) **55ºC**: SP = - 0.25 CD + 11.33; **65ºC**: SP = - 0.27 CD + 13.06;

652 **75ºC**: SP = - 0.16 CD + 14.56; **85ºC**: SP = - 0.16 CD + 17.54

653

654 **Figure 4.** RVA viscosity profile of native starch (control, 0 kJ/g) and modified rice starches
655 as function of milling energy.

656 **Figure 5.** Linear relationships between starch pasting viscosities (PV, SB y VF) and
657 particle size (D_{50}).

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Table 1. Typical parameters of particle size distribution: median (D_{50}), specific surface area (SSA) and dispersion index ("Span"); and thermal properties: enthalpy (ΔH) and peak temperature of gelatinization (Tp); as function of milling energy.

			Particle size distribution			**Thermal properties**	
Energy (kJ/g)	Time[1] (min)	Temp.[2] (ºC)	D_{50} (µm)	SSA (m^2/g)	Span	ΔH (J/g)	T_p (°C)
0	0	0	60.9 ± 10.8^{b}	0.29 ± 0.03^{a}	3.9 ± 0.3^{d}	11.6 ± 0.3^{c}	$76,6 \pm 0.4^{b}$
0.26	5.4	38.0	16.9 ± 0.6^{a}	0.62 ± 0.01^{g}	4.0 ± 0.0^{d}	6.5 ± 0.2^{b}	$74.8 \pm 0.4^{a,b}$
0.52	10.6	45.0	15.5 ± 0.4^{a}	0.58 ± 0.01^{f}	3.1 ± 0.1^{c}	1.5 ± 0.3^{a}	72.5 ± 0.5^{a}
1.04	21.8	50.5	13.4 ± 0.2^{a}	$0.56 \pm 0.00^{c.d.e}$	2.5 ± 0.1^{b}	ND	ND
1.5	31.7	51.5	12.4 ± 0.1^{a}	$0.57 \pm 0.00^{e.f}$	2.3 ± 0.1^{b}	ND	ND
1.99	42	52.2	12.2 ± 0.1^{a}	$0.57 \pm 0.00^{d.e.f}$	2.0 ± 0.1^{a}	ND	ND
2.63	57.4	54.0	12.8 ± 0.2^{a}	$0.55 \pm 0.01^{b.c.d}$	2.0 ± 0.1^{a}	ND	ND
3.56	75.3	54.5	12.9 ± 0.3^{a}	$0.54 \pm 0.01^{b.c}$	1.8 ± 0.0^{a}	ND	ND
4.08	86.9	55.1	13.2 ± 0.3^{a}	0.53 ± 0.01^{b}	1.9 ± 0.1^{a}	ND	ND

[1] Process time using a rotational speed of 400 rpm. [2] Temperature of the sample at the end of the process. The listed values represent the average value from five (particle size distribution) or three determinations (thermal properties) ± standard deviation.

Values in the same column with different letter differs significantly ($p < 0.05$). ND: not detected.

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676 **Table 2:** Water solubility index (WSI) and swelling power (SP) of native and modified rice
677 starches, depending on the specific milling energy (E) and the test temperature.

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	Water solubility index (%)				Swelling power (g/g)			
E	**WSI**	**WSI**	**WSI**	**WSI**	**SP**	**SP**	**SP**	**SP**
(kJ/g)	**55ºC**	**65ºC**	**75ºC**	**85ºC**	**55ºC**	**65ºC**	**75ºC**	**85ºC**
0	0.07 ±0.00^{a,1}	0.94 ±0.19^{a,2}	1.28 ±0.24^{a,3}	1.54 ±0.05^{a,3}	2.12 ±0.05^{a,1}	2.61 ±0.05^{a,2}	5.97 ±0.13^{a,3}	7.43 ±0.13^{a,4}
0.26	3.32 ±0.16^{b,1}	4.19 ±0.08^{b,2}	5.93 ±0.24^{b,3}	6.42 ±0.03^{b,4}	3.74 ±0.06^{b,1}	5.10 ±0.23^{b,2}	9.83 ±0.11^{b,3}	12.72 ±0.50^{b,4}
0.52	5.68 ±0.03^{c,1}	4.16 ±0.31^{b,1}	7.86 ±0.30^{c,2}	8.58 ±0.29^{c,2}	5.69 ±0.10^{c,1}	6.79 ±0.53^{c,2}	10.59 ±0.33^{c,3}	13.46 ±0.84^{b,4}
1.04	10.04 ±0.14^{d,2}	8.76 ±1.00^{c,1}	11.79 ±0.25^{d,3}	13.13 ±0.11^{d,4}	8.03 ±0. 08^{d,1}	9.35 ±0.37^{d,2}	12.29 ±0.13^{d,3}	15.92 ±0.42^{c,4}
1.50	12.54 ± 0.46^{e,1}	13.01 ± 0.14^{d,1}	14.77 ± 0.78^{e,2}	15.09 ± 0.53^{e,2}	8.87 ± 0.02^{e,1}	10.39 ± 0.12^{d,e,2}	12.42 ± 0.06^{d,3}	16.80 ± 0.40^{d,4}
1.99	16.88 ±0.47^{f,1}	15.93 ±1.38^{e,1}	18.74 ±0.61^{f,2}	19.22 ±0.47^{f,2}	9.41 ±0.16^{f,1}	10.92 ±0.67^{e,f,2}	13.49 ±0.17^{e,3}	16.43 ±0.67^{c,d,4}
2.63	20.41 ±0.11^{g,1}	21.13 ±0.62^{f,1}	22.78 ±0.62^{g,2}	23.60 ±0.33^{g,2}	9.89 ±0.14^{g,1}	11.24 ±0.04^{e,f,2}	13.69 ±0.05^{e,3}	16.42 ±0.31^{c,d,4}
3.56	24.13 ±0.62^{h,1}	24.63 ±0.59^{g,1}	26.01 ±0.55^{h,2}	28.20 ±0.30^{h,3}	10.11 ±0.23^{g,h,1}	11.78 ±0.48^{e,f,2}	13.74 ±0.37^{e,3}	17.08 ±0.26^{d,4}
4.08	26.36 ±0.30^{i,1}	25.39 ±3.18^{g,1}	29.08 ±0.08^{i,1,2}	29.70 ±0.42^{i,2}	10.28 ±0.14^{h,1}	11.49 ±1.80^{f,1}	13.93 ±0.91^{e,2}	16.38 ±0.60^{c,d,3}

679 *Results are mean of three determinations ± standard deviation.*

680 *The means in the columns with different letters in the superscript are significantly different from the grinding*
681 *energy ($p < 0.05$). The means in the rows with different numbers in the superscript are significantly different*
682 *from the treatment temperature ($p < 0.05$).*

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692 **Table 3.** Pasting properties of rice starch as function of milling energy.

E (kJ/g)	PT (ºC)	Pt (min)	PV (mPa.s)	BD (mPa.s)	TV (mPa.s)	SB (mPa.s)	FV (mPa.s)
0	79.1 ± 0.1^{d}	6.32 ± 0.03^{e}	4384 ± 17^{h}	1006 ± 40^{e}	3378 ± 43^{h}	2386 ± 71^{g}	5764 ± 46^{h}
0.26	79.6 ± 0.5^{d}	6.20 ± 0.00^{e}	3627 ± 12^{g}	981 ± 26^{e}	2646 ± 14^{g}	2146 ± 38^{f}	4792 ± 24^{g}
0.52	74.3 ± 0.0^{b}	5.90 ± 0.05^{d}	2995 ± 15^{f}	1041 ± 33^{e}	1954 ± 18^{f}	1977 ± 83^{e}	3931 ± 65^{f}
1.04	70.2 ± 0.1^{a}	5.50 ± 0.14^{c}	1895 ± 36^{e}	887 ± 39^{d}	1008 ± 75^{e}	1325 ± 20^{d}	2333 ± 95^{e}
1.50	70.6 ± 1.7^{a}	$5.40 \pm 0.09^{b.c}$	1646 ± 141^{d}	843 ± 62^{d}	803 ± 79^{d}	1144 ± 107^{c}	1947 ± 28^{d}
1.99	76.2 ± 1.7^{c}	5.33 ± 0.09^{b}	1235 ± 49^{c}	734 ± 30^{c}	501 ± 18^{c}	696 ± 0^{b}	1197 ± 18^{c}
2.63	84.8 ± 0.0^{e}	$5.30 \pm 0.05^{a.b}$	913 ± 9^{b}	599 ± 36^{b}	314 ± 27^{b}	571 ± 4^{b}	885 ± 31^{b}
3.56	93.6 ± 1.1^{f}	$5.27 \pm 0.09^{a.b}$	595 ± 15^{a}	410 ± 17^{a}	185 ± 2^{a}	405 ± 28^{a}	590 ± 26^{a}
4.08	94.0 ± 0.6^{f}	5.17 ± 0.05^{a}	544 ± 19^{a}	384 ± 16^{a}	160 ± 4^{a}	366 ± 38^{a}	526 ± 42^{a}

693 The listed values represent the average value from two determinations ± standard deviation.

694 Values in the same column with different letter differs significantly ($p < 0.05$).

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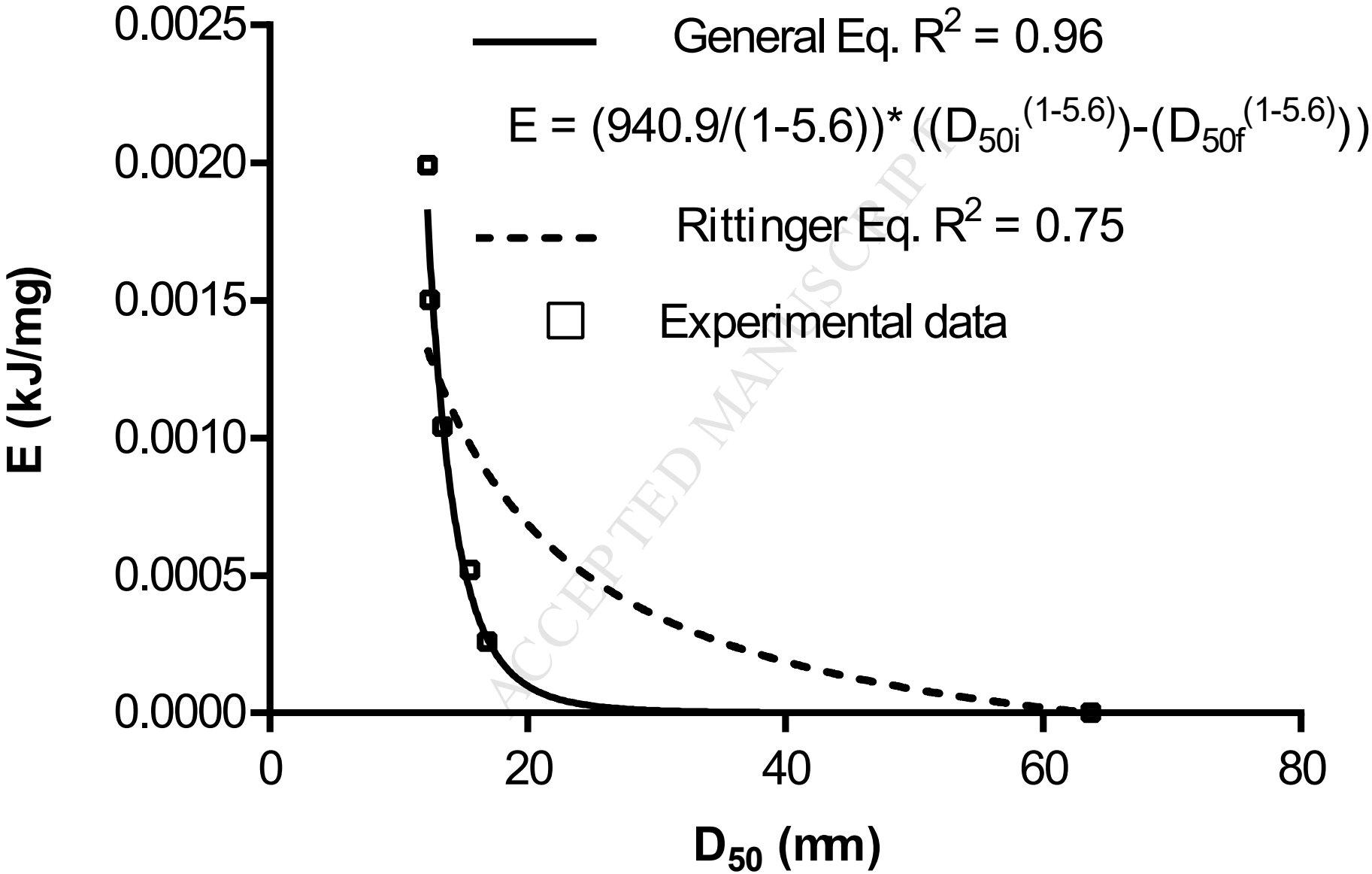

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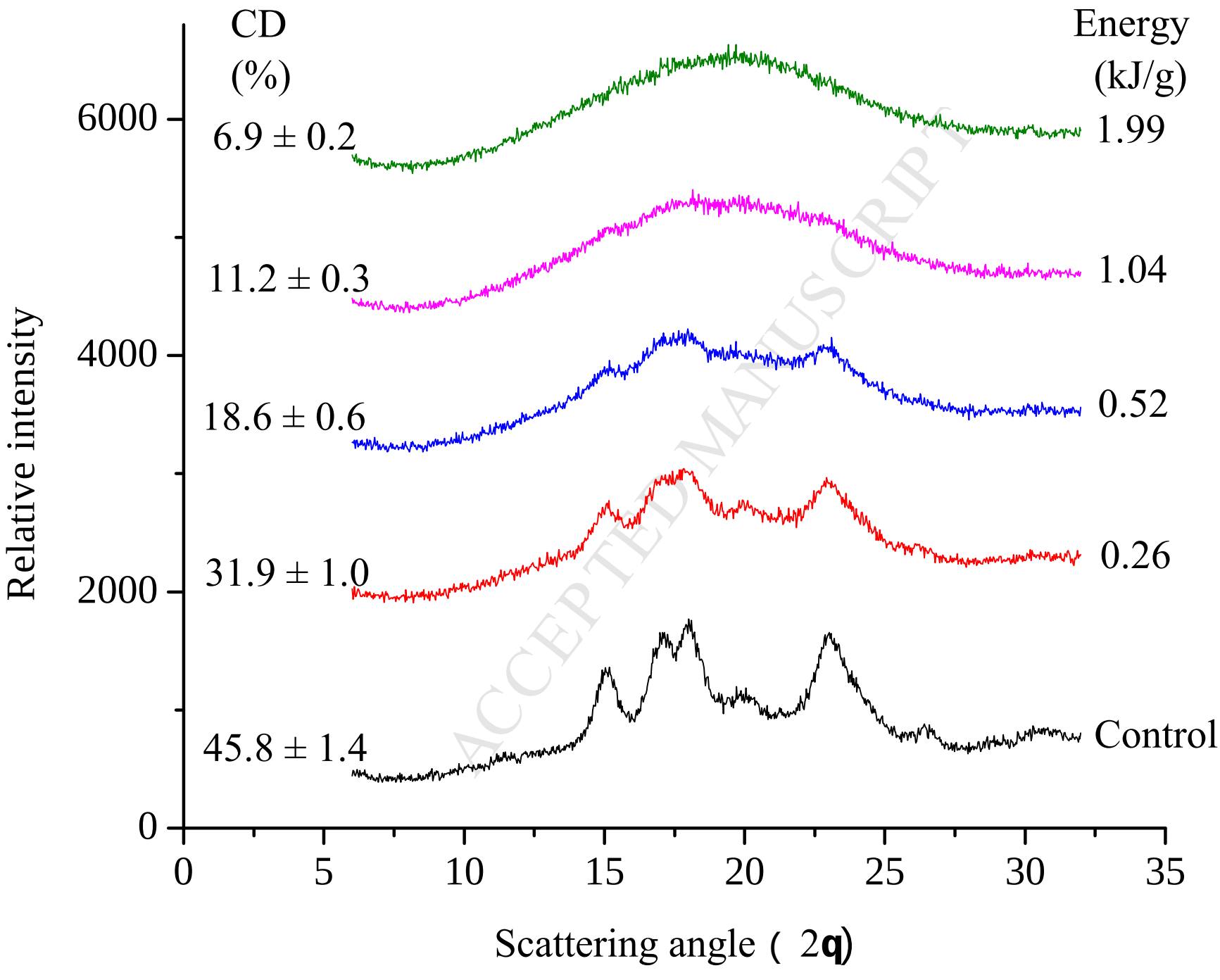

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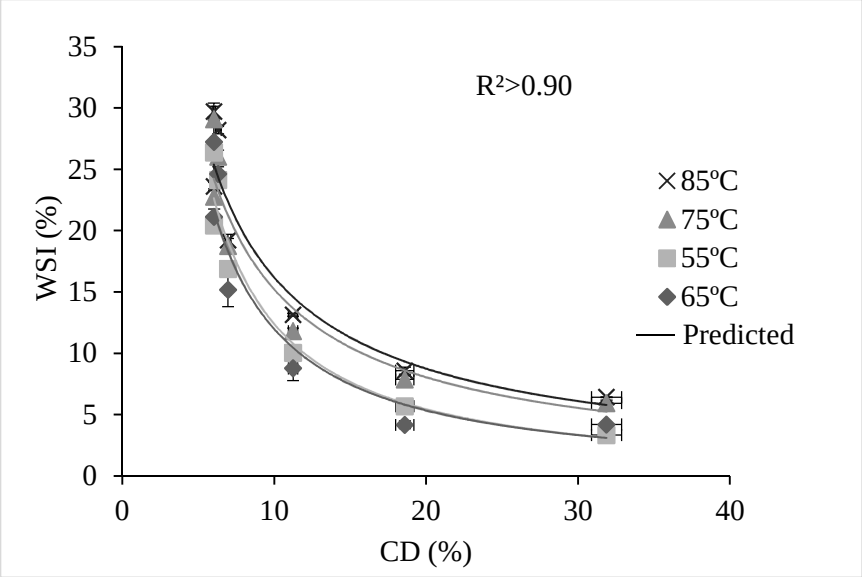

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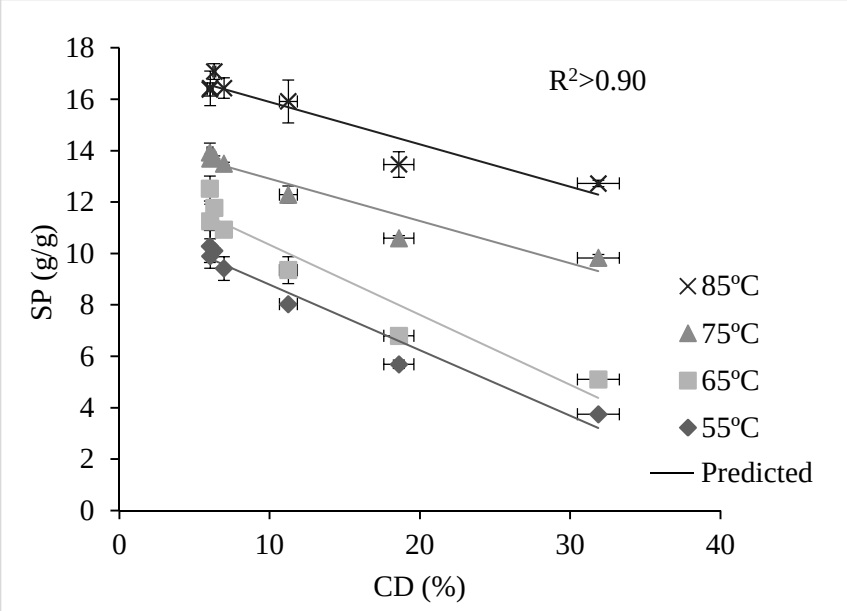

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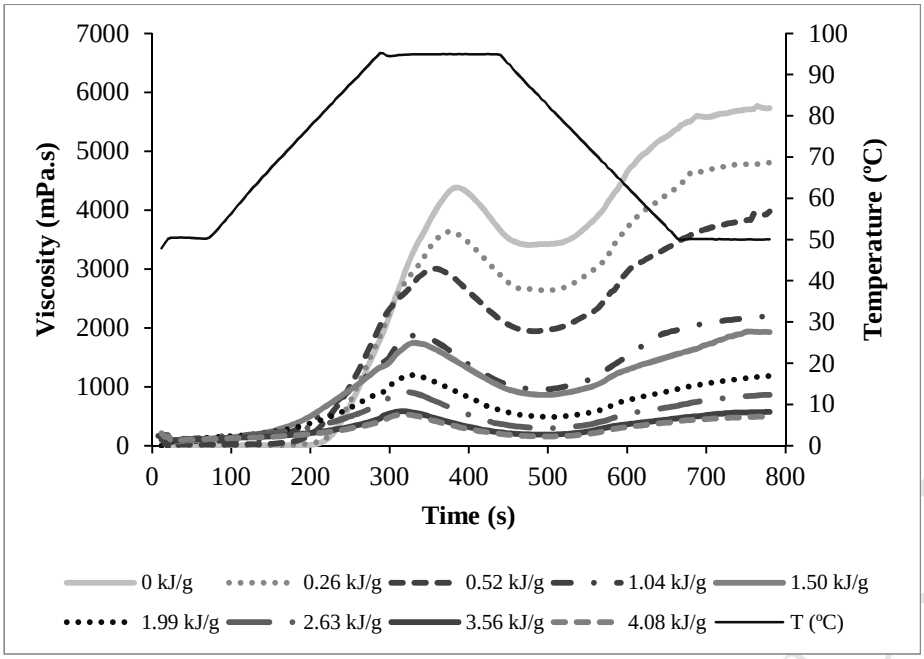

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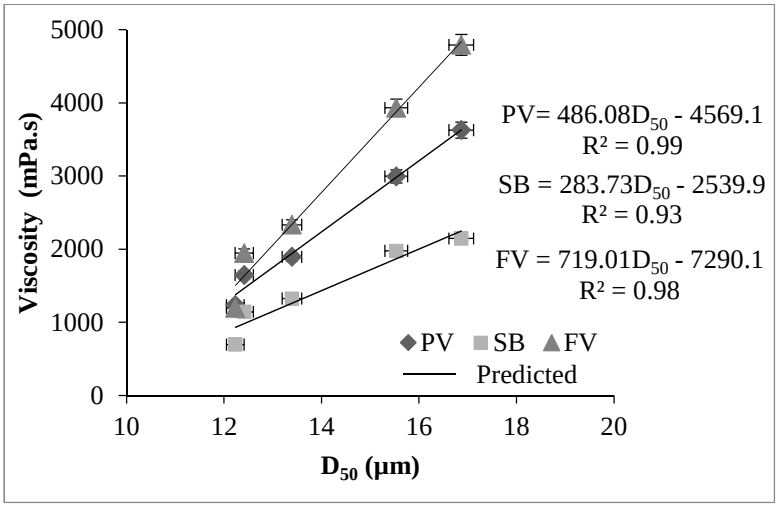

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Highlights

1. Dry milling in planetary ball mill is proposed to modify rice starch properties.
2. Energy-size relationship was accurately predicted by Holmes´ model.
3. Energy was related to physicochemical and functional properties of starch.
4. High impact grinding is an efficient method to modify the structure of starch.
5. Starch with different degrees of gelatinization and crystallinity can be obtained.

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